

NEW SECONDARY BATTERIES UTILIZING ELECTRONICALLY  
CONDUCTIVE POLYMER CATHODES

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## ABSTRACT

The objectives of this project are to optimize the transport rates in electronically conductive polypyrrole films by controlling the morphology of the film and to assess the utility of these films as cathodes in a lithium/polypyrrole secondary battery. During this research period, progress has been made in improving the charge transport rate of the supermolecular-engineered polypyrrole electrode by eliminating the polypyrrole baselayer that hampered earlier work. Also, the fibril density of the polypyrrole electrode was increased, providing more electroactive sites per unit area.

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## I. INTRODUCTION

Polypyrrole is the most attractive polymer for use as a new high-energy-density secondary battery electrode because of its mechanical and electrochemical properties. Polypyrrole has high conductivity, high specific charge density, and reversible electrochemical redox behavior to switch between conducting and nonconducting states.

The objective of this project is to develop a new secondary battery utilizing electronically conductive polypyrrole. To accomplish this objective, it is necessary to gain a better understanding of dynamic behavior within the PPy films and to provide guidance toward designs of new secondary batteries based on this polymer as a cathode material.

This project is a joint project under the direction of Charles R. Martin (Department of Chemistry) and Ralph E. White (Department of Chemical Engineering). This is a joint effort because of the complementary nature of the work done by the co-principal investigators. Martin and his group provide the experimental expertise and White and his group provide data analysis and mathematical modeling expertise.

## II. PROGRESS IN MARTIN'S GROUP

The progress made in Martin's group consists of two parts. A study of the charge transfer rate and charge density of polypyrrole fibrils made from aluminum oxide filters is included in Appendix A. Studies concerning the elimination of the polypyrrole baselayer and battery applications will also be discussed.

### A. Preparation of Polypyrrole with Enhanced Charge Transport

Polypyrrole with a fibrillar/microporous morphology was synthesized by electropolymerization of pyrrole in a host membrane. Chronocoulometry was used to evaluate the charge transport characteristics of the fibrillar/microporous and conventional polypyrrole films. The fibrillar/microporous films exhibited superior electrochemical properties in terms of both charge transport and charge capacity. A detailed discussion of this work is provided in Appendix A.

### B. Baselayer Elimination and Battery Applications

Polypyrrole has been the subject of much investigation as an electrode in secondary lithium batteries (1-6). Of particular interest in this application is the relatively high doping level of the polymer and the possibility of switching the polymer quickly and reversibly from a conducting (oxidized) form to a nonconducting (reduced) form. When oxidizing or reducing polypyrrole, the rate determining step is counterion diffusion. Either the anions corresponding to oxidized pyrrole sites have to move in and out of the film, or cations from the electrolyte solution have to move in and out of the film to maintain charge balance. In a thick film of amorphous polypyrrole, conductivity is lower and kinetics are slower than in a thin film. Also, charge trapping occurs as oxidized pyrrole sites are isolated by proximate polymer chains. As a result, the polymer cannot become fully doped. This would be undesirable in a battery system.

Previous research in this laboratory (7) has shown that when polypyrrole is grown in fibrillar form, the fibrils produce a faster charge transfer rate and a higher doping level than an amorphous film of comparable thickness. Fibrillar forms of polypyrrole were grown by electropolymerization of pyrrole in the pores of a host membrane which was stretched across a platinum electrode and held in place by a rubber sheath. The host membrane was then dissolved, leaving behind the polypyrrole fibrils standing upright on the electrode surface (Fig. 4). Following this work, attempts have been made to improve the performance of these electrodes by making the diameter of the fibrils smaller. Although the performance of the smaller diameter fibrils was an improvement over that of the film, the current density and charge capacity did not increase proportionately with decreasing fibril diameter as expected. This could be because of the growth of a baselayer of polypyrrole between the porous host membrane ('e' of Fig. 5) and the platinum substrate ('g' of Fig. 5) of the electrode. For  $0.2\text{ }\mu\text{m}$  fibrils, this layer was as thick as  $0.3 - 0.5\text{ }\mu\text{m}$ .

It is logical to assume that a baselayer of polypyrrole thicker than the fibril itself would serve to negate the advantages of fibrillar morphology. Since the baselayer would have to be reduced and oxidized as well as the fibrils, the switching reaction rate of the entire film would be slowed. We have been working to improve electrode/polymer adhesion by sputtering and vapor depositing gold directly on the porous membrane, thereby eliminating the layer of solution between the host membrane and the platinum electrode and preventing base layer formation. Figure 1 is a Schematic of a section of the electrode I have been using. The membrane is attached to a section of glass tubing to hold it flat, then sputtered with gold. More gold is vapor deposited on top. Contact is made with silver epoxy and a copper wire, then Torr Seal, an inert epoxy, is used to seal the electrode and make it mechanically stable. Polypyrrole is then grown galvanostatically through the pores in the host membrane, and the membrane

is extracted. To determine that the pores in the host membrane were completely covered by sputtered gold, electron micrographs were taken of membranes with varying thicknesses of gold deposited on them. Figures 2-4 are a series of electron micrographs with 100Å, 600Å, and 900Å of gold deposited on them, respectively. Pores are no longer visible in Fig. 4. Also, a spot test with a highly colored ion,  $\text{Ru}(\text{bpy})_3$ , was performed. The ion did not leak through the membrane, indicating that the pores were completely covered. Pores of 1000Å diameter with 7000Å of gold vapor deposited on them also passed the electron microscopy and spot tests. Electrodes were made, and polypyrrole was grown. Figure 5 is an electron micrograph of polypyrrole fibrils on a gold surface. Figure 6 is a charge/time transient from a potential step experiment performed with the electrode.

One drawback of using Nuclepore as a host membrane is that the pore density does not increase proportionately with decreasing pore diameter. As can be seen in Table 1, the electroactive area of an electrode made with a Nuclepore membrane with pore diameters of 0.01 microns is only 0.02% of the geometric area. Another company, the Poretics corporation, can make membranes of much higher pore densities. Figure 7 is an electron micrograph of a Poretics membrane of with a pore density of  $10^{10}$  pores/cm<sup>2</sup>, which is two orders of magnitude higher than the highest pore density offered by the Nuclepore Corporation. We are now conducting fundamental investigations of the effect of pore diameter on the charge transfer rate of fibrils prepared from Nuclepore and Poretics membranes, and we are also considering other substrates such as etched mica and an aluminum oxide filter made by the Anapore Corporation. A study of the charge transfer rate and charge capacity of polypyrrole fibrils made from the aluminum oxide filters is included in Appendix A.

A battery has been built using the Anapore aluminum oxide membranes for a template to grow polypyrrole fibrils. It shows much better adhesion to the sputtered

gold layer than either the Nuclepore or Poretics polycarbonate membranes. Capacitance studies revealed that the actual electroactive area for an electrode made with polycarbonate membranes sputtered with gold was much higher than the electroactive area calculated from the pore diameter and pore density. This indicates that there is some separation between the polycarbonate membrane and the sputtered gold layer on the back. Such a separation would encourage formation of a polypyrrole base layer upon electrochemical polymerization. Anapore's aluminum oxide membranes have a total pore area of over 60%, which is much higher than the total pore area of the Poretics membranes. Thus, Anapore membranes would produce more polypyrrole sites per unit geometric area of the current collector. For this reason, Anapore membranes were chosen for preliminary battery studies. The anode is a lithium metal disk pressed onto a platinum disk current collector, with electric contact made with silver epoxy and a copper wire. The electrolyte used was vacuum-dried 1M  $\text{LiClO}_4$  in vacuum-distilled propylene carbonate. Pyrrole was distilled under nitrogen before use. Pyrrole was polymerized galvanostatically, then the pyrrole-containing solution in the cell was replaced with fresh electrolyte. Cyclic voltammograms were taken (Fig. 10) before and after 10 cycles of potential step experiments. An example of a charge/time transient from a potential step experiment is shown in Fig. 11. An electron micrograph of the polypyrrole taken after experimentation and extraction of Anapore is shown in Fig. 12. Note that the fibril density is much higher than that of earlier electrodes made with Nuclepore membranes.



### III. PROGRESS IN WHITE'S GROUP

The progress made in White's group over the past year consists of two parts. To gain a better understanding of the dynamic behavior within the electronically conductive polypyrrole film and to provide guidance towards designs of new secondary batteries based on the polypyrrole as a cathode material, comprehensive mathematical models for the cyclic voltammetry of polypyrrole in a one-compartment cell and for the charging/discharging characteristic of a lithium/polypyrrole (Li/PPy) secondary battery cell are developed.

#### A. Cyclic Voltammetry of Polypyrrole

A mathematical model for predicting potentiostatically controlled cyclic voltammograms for a polypyrrole films has been developed earlier. The model was developed within a one-compartment cell with a platinum rotating disk electrode coated with polypyrrole films. Current density, concentrations, stored charge, and electrochemical potential, within the polypyrrole films are predicted as a function of applied potential. Because cyclic voltammetry well presents polypyrrole's redox behavior, this model was used to elucidate the electrochemical reaction mechanisms and the charge transport phenomena within the polypyrrole films by studying the effect of various characteristic parameters. A technical paper on this work has been published in the *Journal of the Electrochemical Society*, **135**, p 1971.

#### B. Lithium/Polypyrrole Secondary Battery

A mathematical mode for simulating charging/discharging processes of the Li/PPy secondary battery system has been developed. This model was used to characterize charging/discharging processes and optimize cell performance by studying the effect of



various design parameters. This model can provide guidance toward designs of new high-energy-density Li/PPy secondary battery cell. A technical paper describing this work has been submitted to the *Journal of the Electrochemical Society* for publication and is included in this report as Appendix B.

#### IV. FUTURE STUDY

During this research period, a better understanding has been gained of the fundamental electrochemical process within the polypyrrole film. Future work in this area will be completing previous work and optimizing lithium/polypyrrole secondary battery cell performance based on the previous studies.

##### A. Martin's Group

Future work will be concentrated on experimentation with the Li/LiClO<sub>4</sub>/PPy secondary battery cell and collaboration with the model being developed in White's group. We are currently working to improve the reproducibility of the fibril growth so that a verifiable correlation can be obtained between charge passed during polymerization and fibril length. When this is achieved, charge/time transients of different fibril lengths can be recorded and the results compared to flat polypyrrole films. After reproducible data is obtained, charge/discharge experiments using the battery cell can be performed and the energy densities compared to those of the recent work of others (1). Investigation of another conductive polymer such as polythiophene or poly-3-methylthiophene for battery applications is also desirable, as well as fundamental studies on a new polymer, polyphosphazine.

##### B. White's Group

It is desired to continue a detailed study of the electrode mechanisms and transport phenomena which affect the performance of the polypyrrole electrode process. Parameter estimation techniques can be combined with previously developed mathematical models. Interesting parameters (electrochemical reaction rate, diffusion coefficient, etc.), which characterize transport processes and kinetic mechanisms, can be estimated

from the statistical comparison of model predictions to experimental data which will be prepared by Martin's group. The results can be used to predict performances of a variety of electrode designs, and should lead to optimal morphology of the polypyrrole cathode in the secondary battery cell.

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Table I. Nuclepore membrane data.

pore diameter $\mu\text{m}$	pore density per $\text{cm}^2$	% area in pores
12.000	$1.0 \times 10^5$	11.31
10.000	$1.0 \times 10^5$	7.85
8.000	$1.0 \times 10^5$	5.03
5.000	$4.0 \times 10^5$	7.85
3.000	$2.0 \times 10^6$	14.14
2.000	$2.0 \times 10^6$	6.28
1.000	$2.0 \times 10^7$	15.71
0.800	$3.0 \times 10^7$	15.08
0.600	$3.0 \times 10^7$	8.48
0.400	$1.0 \times 10^8$	12.57
0.200	$3.0 \times 10^8$	9.42
0.100	$3.0 \times 10^8$	2.36
0.080	$3.0 \times 10^8$	1.51
0.050	$3.0 \times 10^8$	0.59
0.030	$3.0 \times 10^8$	0.21
0.015	$3.0 \times 10^8$	0.05
0.010	$3.0 \times 10^8$	0.02

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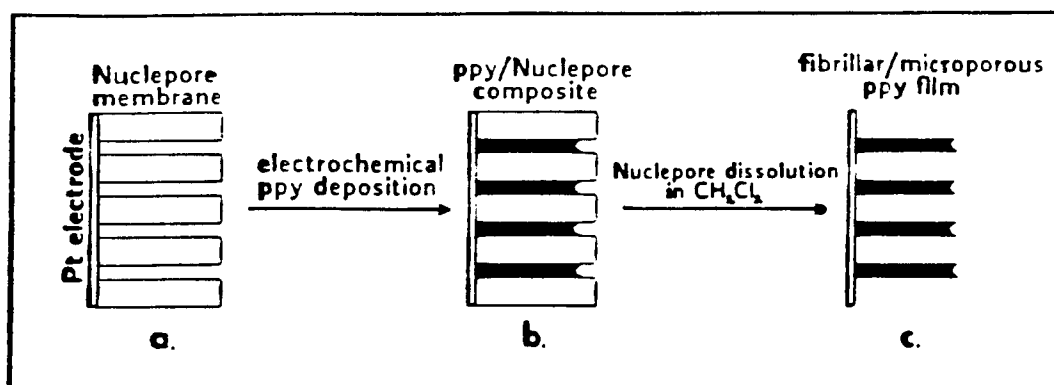


Fig. 1. Schematic diagram of the procedure for preparing fibrillar-microporous conducting polymer films.

- a. 7mm glass tube
- b. Cu wire
- c. Kel-F electrode body
- d. Ag epoxy contact
- e. convex Pt disk
- f. rubber collar
- g. Nuclepore membrane

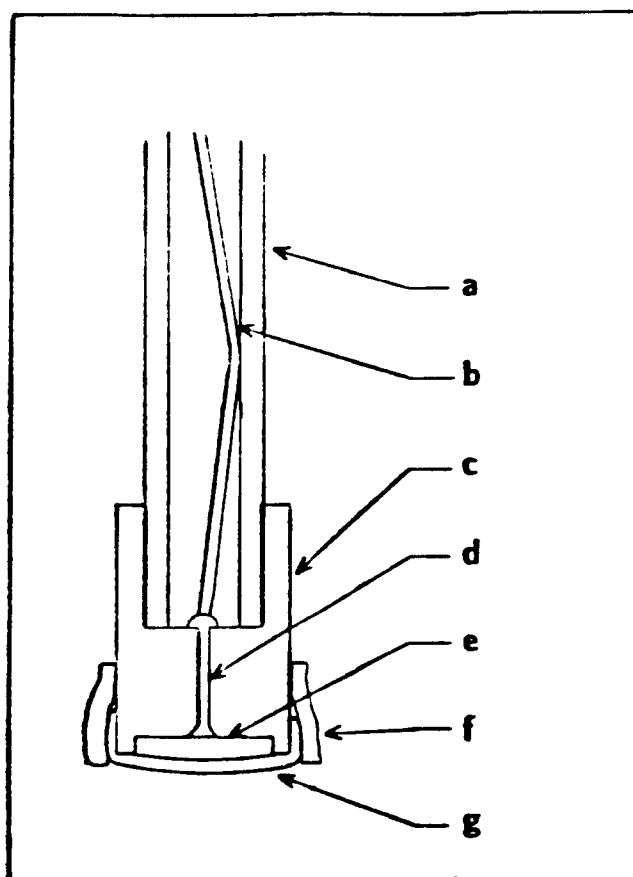


Fig. 2 Schematic diagram of Nuclepore-modified electrode employed for preparing fibrillar polypyrrole films.

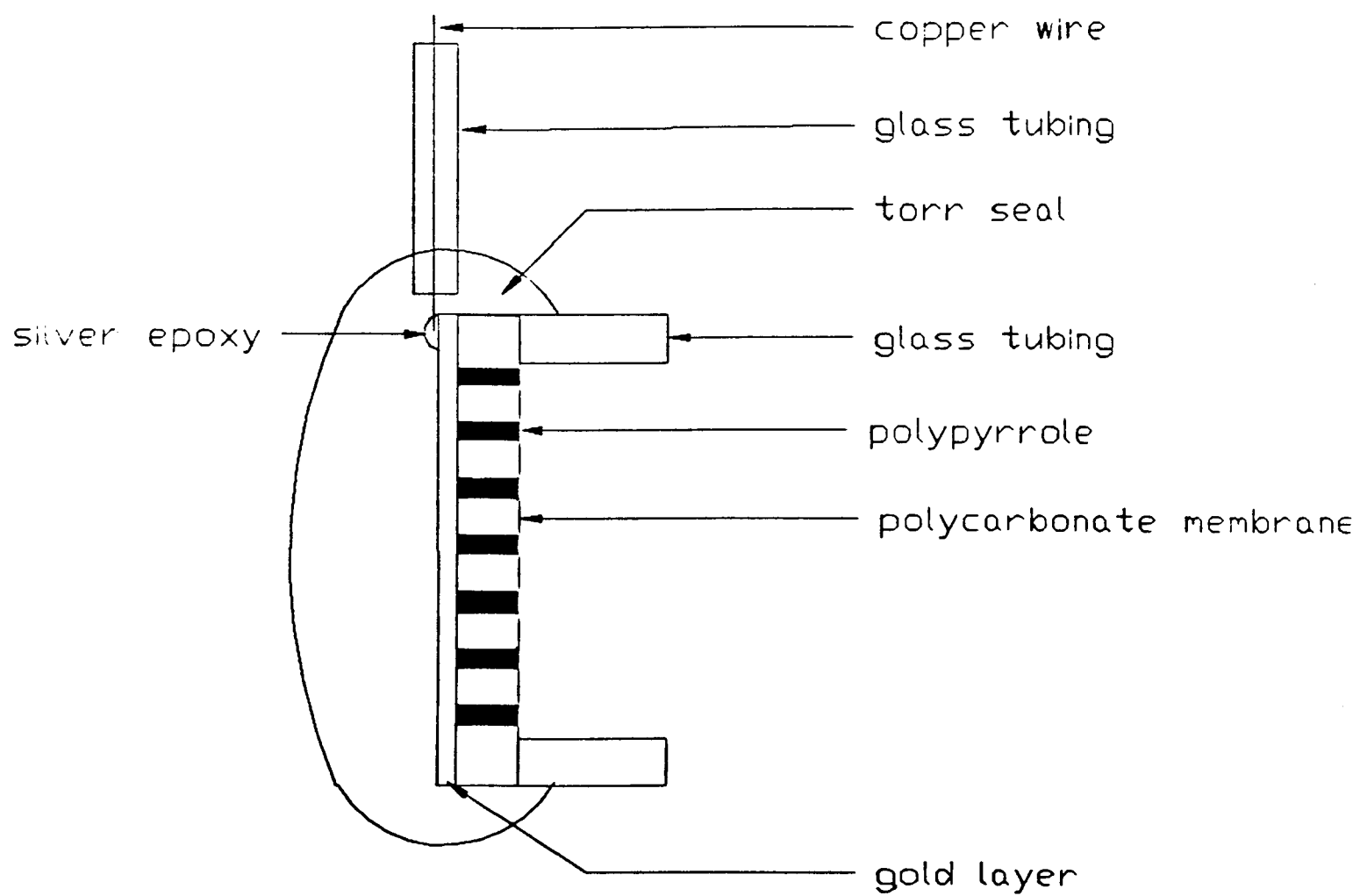


Fig. 3 Cross-section of fibrillar polypyrrole electrode.



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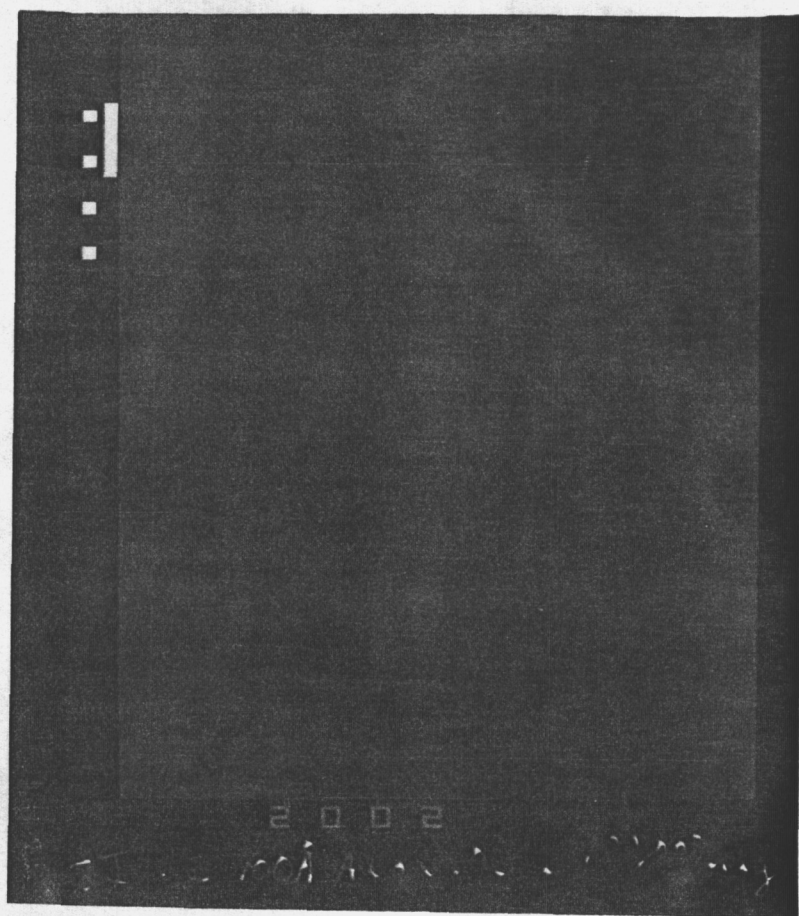


Fig. 4 Nuclepore polycarbonate membrane with  $0.03\ \mu\text{m}$  pore diameter and  $0.01\ \mu\text{m}$  sputtered Au at  $100,000\times$  magnification.

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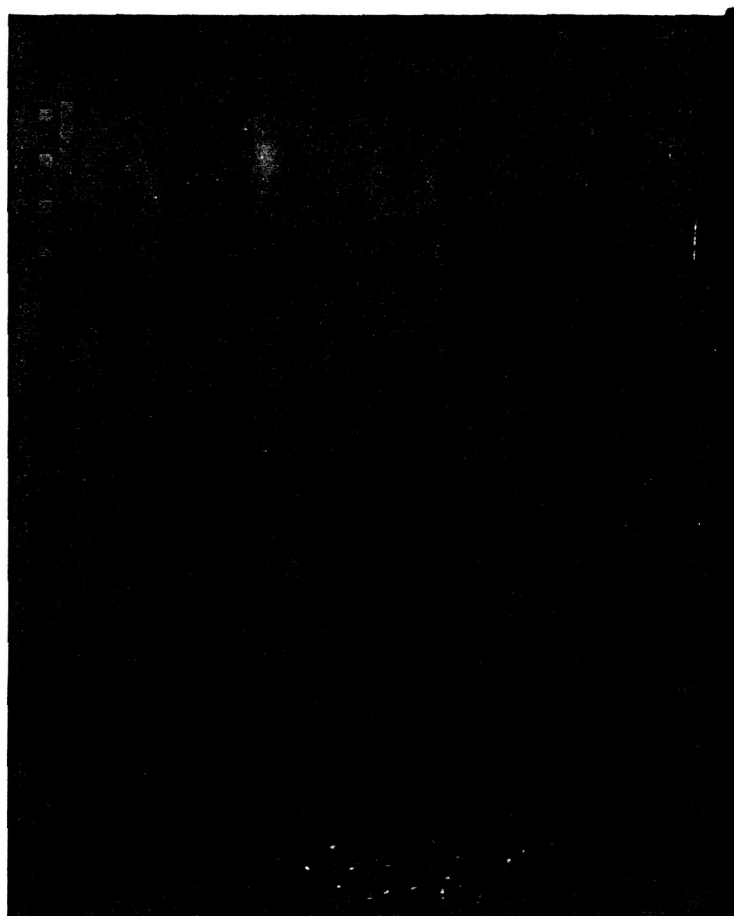


Fig. 5 Nucleopore polycarbonate membrane with  $0.03\ \mu\text{m}$  pore diameter and  $0.06\ \mu\text{m}$  sputtered Au at  $100,000\times$  magnification.

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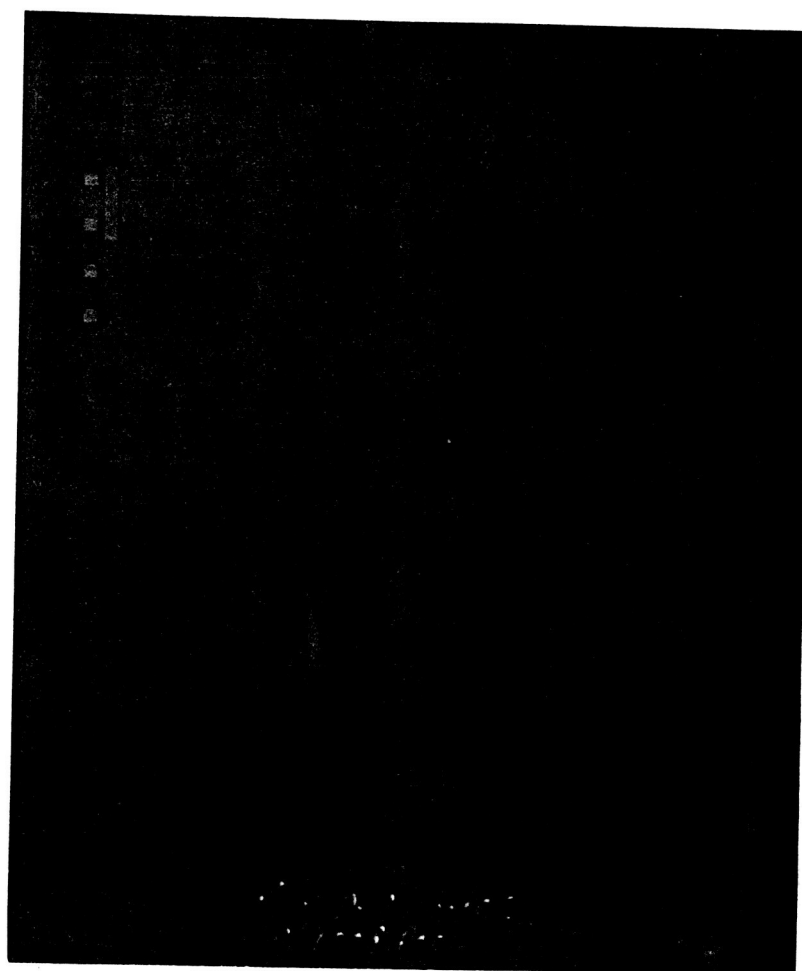


Fig. 6 Nucleopore polycarbonate membrane with  $0.03\ \mu\text{m}$  pore diameter and  $0.09\ \mu\text{m}$  sputtered Au at  $100,000\times$  magnification.

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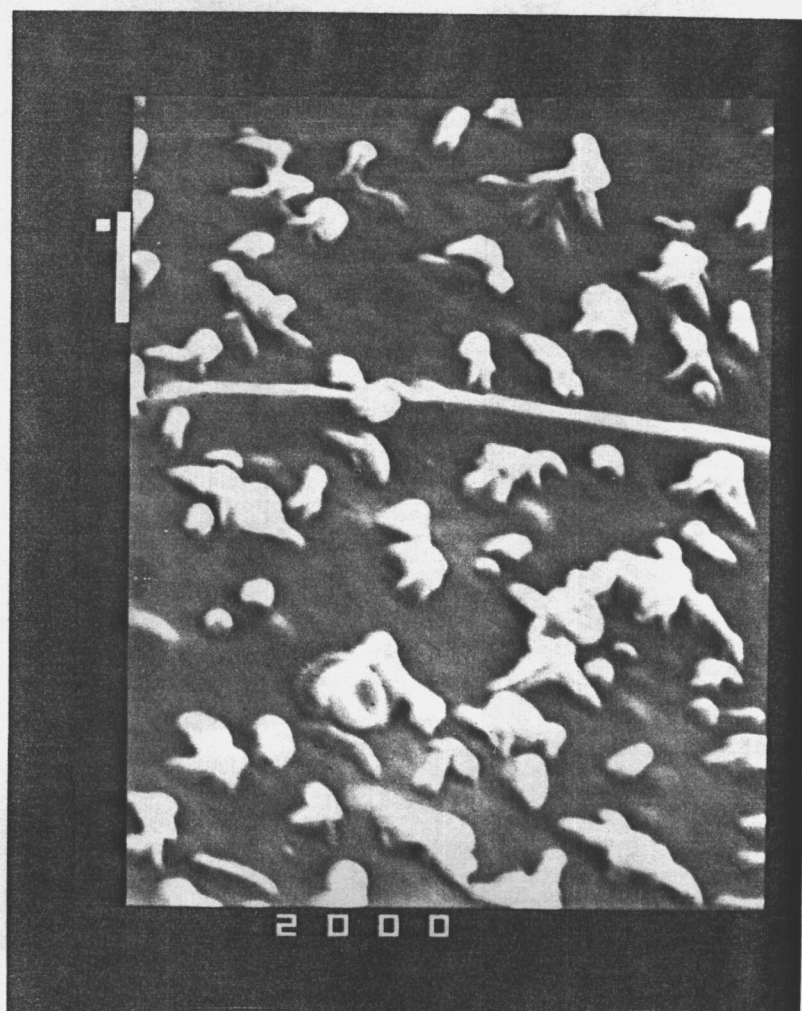


Fig. 7 Fibrillar polypyrrole on a Au surface with polycarbonate membrane extracted.  $1.5 \text{ cm} = 1.0 \mu\text{m}$ .

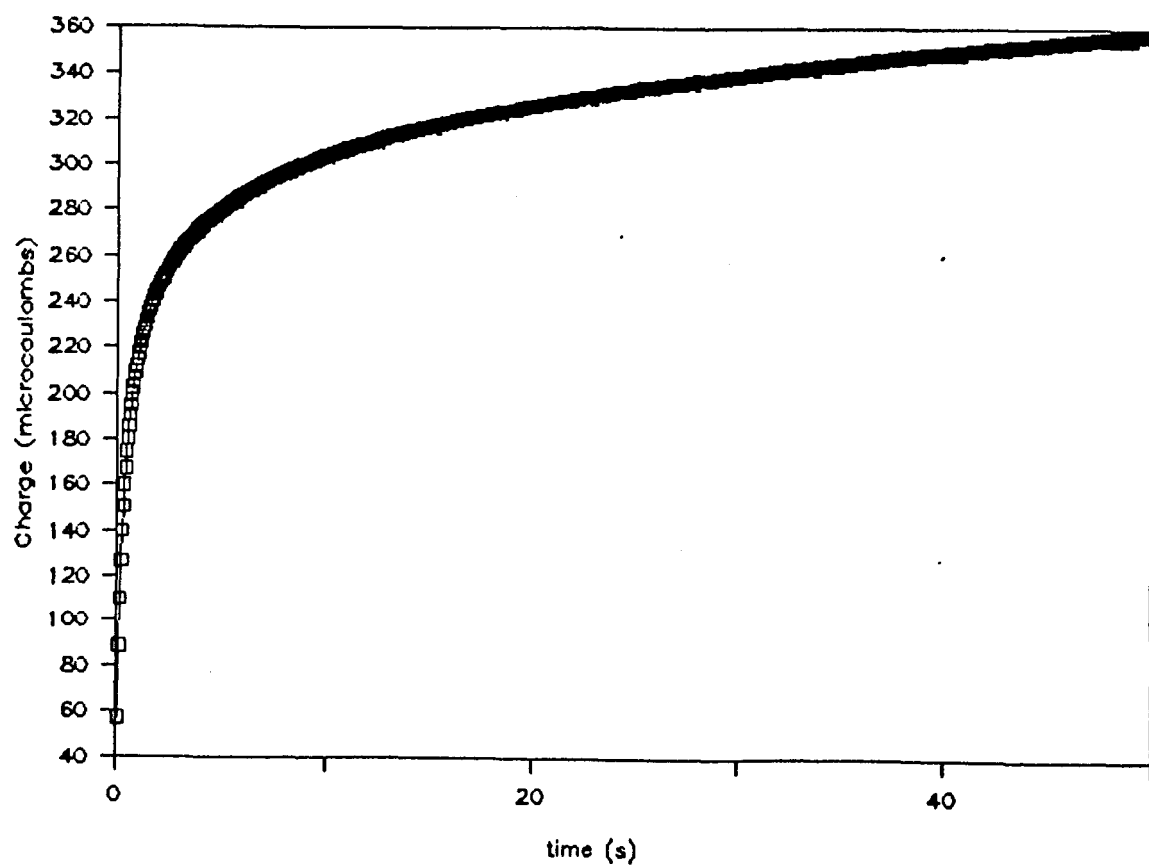


Fig. 8 Charge/time transient of fibrillar polypyrrole electrode grown with  $0.1\ \mu\text{m}$  Nuclepore membrane.

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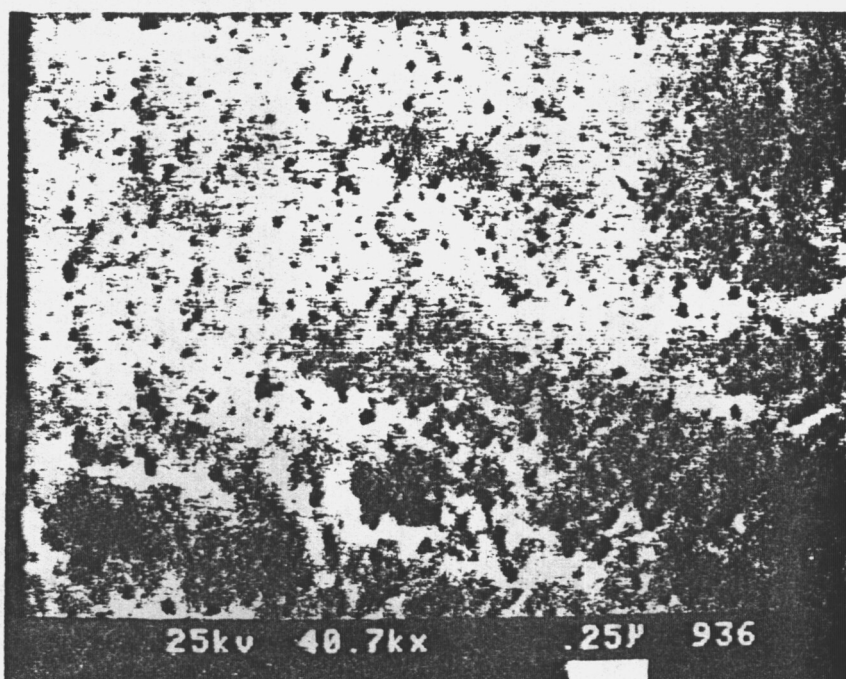


Fig. 9 Electron micrograph of high density ( $\sim 10^{10}$  pores/cm<sup>2</sup>) Poretics membrane. 1 cm = 0.25  $\mu$ m.

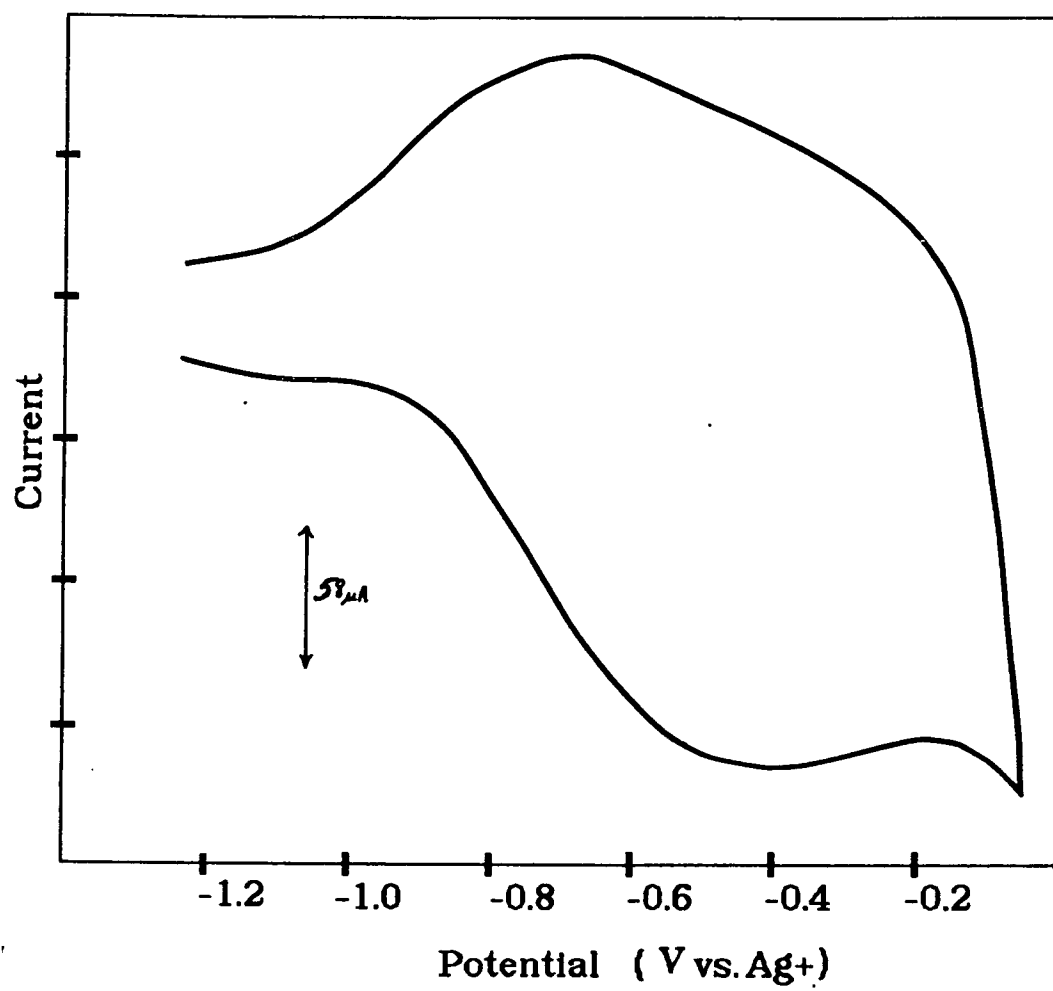


Fig. 10 Cyclic voltammograms of polypyrrole/Anapore composite.

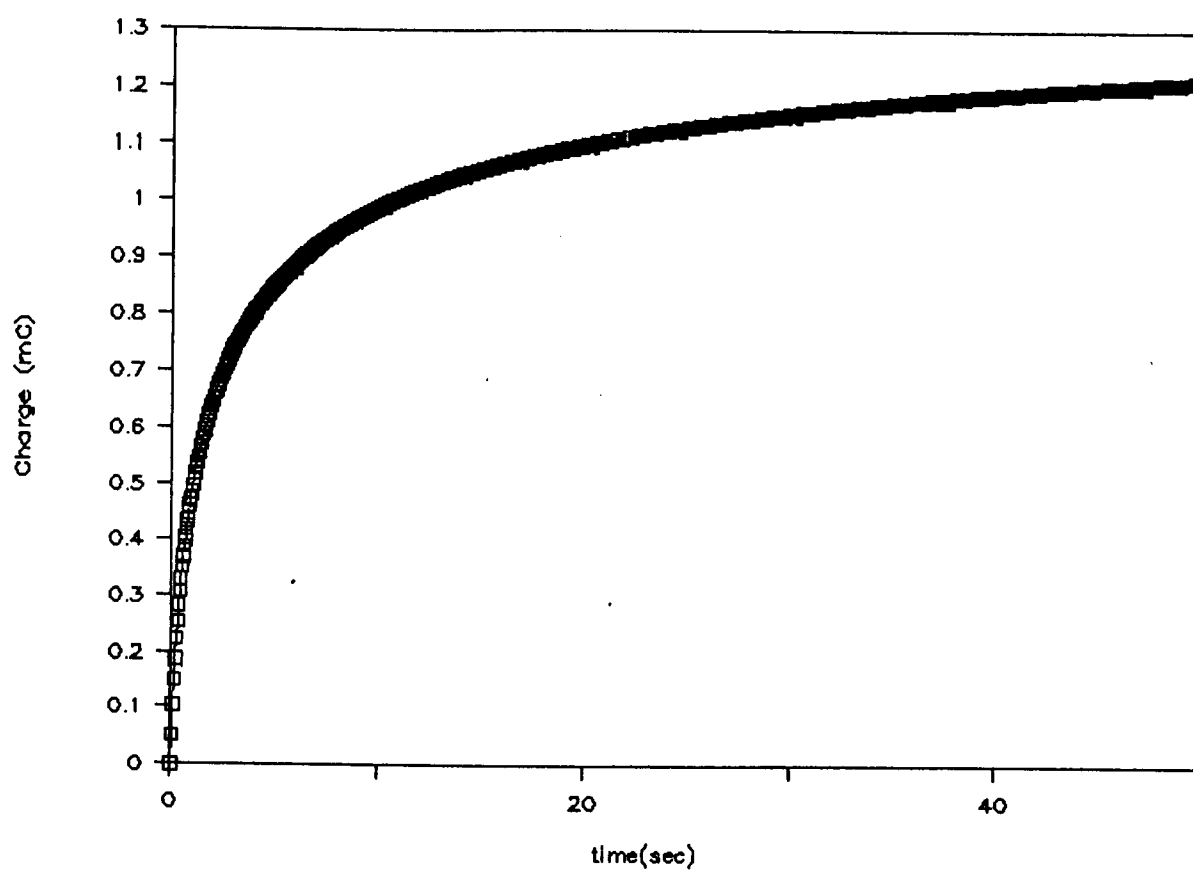


Fig. 11 Charge/time transient of fibrillar polypyrrole grown with Anapore membrane in battery cell.



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Fig. 12 Electron micrograph of polypyrrole battery electrode grown with Anapore membrane in battery cell.

## APPENDIX A

### PREPARATION OF AN ELECTRONICALLY CONDUCTIVE POLYMER WITH ENHANCED CHARGE TRANSPORT

PREPARATION OF AN ELECTRONICALLY CONDUCTIVE POLYMER  
WITH ENHANCED CHARGE TRANSPORT

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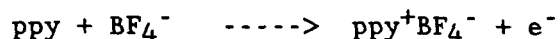
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## Introduction

Electronically conducting polymers are a class of materials which are presently the subject of intense research by the scientific community (1). One of the most interesting features of these polymers is the ability to repeatedly switch them between insulating and conducting states. This redox switching of the polymer is responsible for many of the proposed applications of these materials such as battery cathodes (2), elements in molecular electronics (3), and as electrochromic devices (4). In the case of polypyrrole the redox reaction can be written as



where ppy is the reduced form of polypyrrole,  $\text{BF}_4^-$  is a charge compensating counterion, and  $\text{ppy}^+$  is the oxidized form of polypyrrole. It is important to note that during the redox switching counterions must be incorporated into or expelled from the polymer film to maintain charge neutrality in the polymer. It is thought that the kinetics of the switching process are limited by counter-ion transport in the polymer film(5). This ion transport is very slow and decreases with increasing polymer film thickness. We have recently measured  $D_{\text{app}}$  in thin reduced polypyrrole films to be on the order of  $10^{-9} \text{ cm s}^{-1}$  (6). Moreover the reduction of polymer redox kinetics is accompanied by a decrease in the specific charge capacity of the film with respect to the theoretical charge capacity. This phenomenon known as "charge trapping" occurs when oxidized polymer sites become surrounded by insulating polymer and thus become electrochemically isolated (7).

Therefore if faster switching rates are to be obtained in electronically conductive polymers, the rate of ion transport in the polymer must be increased. The slow ion transport in polypyrrole is a result of its very dense amorphous morphology. We believe this morphology is very poor for

fast ion transport and that controlling the morphology of the polymer is key in enhancing charge transport rates. Penner and Martin (8,9) and Naoi and Osaka (10) have previously shown that charge transport in polypyrrole can be enhanced by controlling the morphology of the polymer. We believe that a fibrillar/microporous morphology similar to that of polyacetylene (11) is the best morphology for ionic transport. This will be explained in the results and discussion section. In this paper a procedure for producing polypyrrole films with a well-defined transport optimized morphology is presented. This procedure involves the electrochemical polymerization of polypyrrole into a host membrane which serves as a template for the growth of the polymer. The membrane is then extracted away leaving a polypyrrole film with the desired fibrillar/microporous morphology. Electrochemical data for conventional polypyrrole and polypyrrole prepared via this procedure are presented. The fibrillar/microporous polypyrrole prepared in this manner shows both enhanced charge-transport properties and increased charge capacity.

## Experimental

All electrochemical measurements were accomplished using a EG&G PAR Model 273 potentiostat/galvanostat driven by Headstart electrochemical software running on an IBM PS/2 Model 50 personal computer. Scanning electron micrographs were obtained with a JEOL JSM-25SII SEM in secondary electron mode at an accelerating voltage of 25 KeV. UV-Vis reflectance spectra were obtained with a Perkin-Elmer Lambda 4B spectrophotometer equipped with an integrating sphere attachment.

## Electrodes and Electrochemical Cells

Anopore  $\text{Al}_2\text{O}_3$  membranes with 0.2 micron diameter pores were used as the host membrane. The membranes were made conductive by sputter coating one side with ca. 500 angstroms of Au using a Technics argon plasma sputter coater. Electrical contact was made to the membrane by silver epoxying (Epotek 410E) a copper wire to the sputter coated Au. Gold was then electroplated onto the conductive side of the membrane from a commercial plating solution (Orotemp 24, Technic Inc.). The electroplating was done galvanostatically at a current density of  $2 \text{ mA/cm}^2$  until a pinhole free gold coating was formed (approximately 5 minutes). Epoxy (Torr Seal, Varian) was used to mask off the electrode leaving an active area of approximately  $0.5 \text{ cm}^2$ . This electrode is shown in figure 1. Platinum disk ( $0.5 \text{ cm}^2$ ) electrodes were constructed as before(6). A large area  $\text{SnO}_2$  coated glass electrode was used to prepare polypyrrole films for the spectroscopic studies. All electrochemical studies were done in conventional one compartment electrochemical cells employing a Pt counter electrode and a conventional saturated calomel reference electrode (SCE). All solutions were degassed by purging with  $\text{N}_2$ .

## Polypyrrole film deposition

Polypyrrole films were grown galvanostatically at a current density of  $i = 1 \text{ mA/cm}^2$  from 0.5M pyrrole in 0.2M  $\text{Et}_4\text{NBF}_4$  in acetonitrile. Film thicknesses were calculated from the charge passed during the polymerization. The relationship used was that  $378 \text{ mC/cm}^2$  were required to produce a  $1.0 \mu\text{m}$  thick film (6). For the Anopore electrodes the current

density was normalized to the electroactive area of the membrane (ie. the gold exposed at the base of the pores). All reagents were purified as previously described (6). The Anopore membrane was extracted by soaking in 0.2M NaOH for 15 min. The electrode was then soaked for 3 minutes in 0.5M H<sub>2</sub>SO<sub>4</sub> to restore proton activity to the film. The electrochemical characterization of the films was carried out in a solution of 0.2M Et<sub>4</sub>NBF<sub>4</sub> in acetonitrile.

Cyclic voltammetry was used to inspect the quality of the polypyrrole films. Potential step chronocoulometry was used evaluate charge transport in the polymer films. The initial potential was -0.6V vs SCE and the final potential was +0.2V vs SCE for the oxidation step and vice-versa for the reduction step. The electrode was potentiostatted at the initial potential for a period of several minutes before each step to insure complete oxidation/reduction of the polymer film.

## Results and Discussion

Figure 2 shows a scanning electron micrograph of an Anopore membrane with 0.2 $\mu$ m diameter pores. Anopore is an aluminum oxide membrane made by a patented electrochemical oxidation procedure. It has several unique characteristics which make it an ideal host membrane for these studies. It is mechanically stable, approximately 50 $\mu$ m thick, and has an extremely high density of uniform cylindrical pores. Approximately 60% of the surface is covered with pores. This pore density is much higher than that of other membranes with similar pore structures. Since the amount of polymer which can be deposited in a given volume is controlled by the pore density, a high pore density is necessary to deposit a compact polymer film. This is very

important in battery applications where energy density in terms of both weight and volume is critical. Figure 3 shows the fibrillar/microporous morphology of polypyrrole electropolymerized in Anopore. A high density of uniform polymer fibrils is produced.

Figure 4 shows the typical cyclic voltammetry of a conventional polypyrrole film both as grown and after treating with the base/acid extraction procedure. Note that after the film is treated with the extraction procedure  $E_{pk,an}$  is shifted negative by approximately 220mV. Also  $\Delta E_{peak}$  decreases from ca. 160mV to ca. 80mV. While the peak currents are also decreased, the total charge passed during the voltammogram remains approximately the same. The voltammogram for an equivalent amount of polypyrrole in the fibrillar/microporous form looked identical to the voltammogram of the conventional polypyrrole film after treating with the extraction procedure. It is obvious that the extraction procedure is having an effect on the electrochemistry of the polypyrrole.

Strong bases are known to deprotonate the polymer. However, it has also been shown that the polymer becomes reprotonated upon treating with strong acids (12). It may be that the polymer is not being completely reprotonated with our procedure or that  $SO_4^{2-}$  is being incorporated into the film. The UV-Vis reflectance spectra for the oxidized form of polypyrrole before and after treatment with the extraction procedure are shown in figure 5. These spectra are virtually identical.

Figure 6 shows the current time transients for the oxidation and reduction of a conventional as grown 1.0 $\mu$ m thick polypyrrole film. The extraction procedure had no significant effect on these transients. There are several things to notice on this graph. First the overall rate for



oxidation of the polymer is faster than the rate for reduction. The rate of oxidation is initially lower than that of the reduction. This is to be expected since at the beginning of the oxidation the electrode is covered with a electronically and ionically resistive film. At the beginning of the reduction step the electrode is conductive and one effectively has a porous metal electrode with a very large capacitance. Thus much of the charge which flows during the initial portion of the reduction is capacitive in nature. As the oxidation or reduction continues these features of the polymer become reversed to the point where the reduction finally becomes slower than the oxidation. The total amount of charge passed during the reduction process is also reproducibly lower than that of the for the oxidation. Figure 7 shows the corresponding processes for the fibrillar/microporous version of the film. Notice that the charge-time transients for the oxidation and reduction are virtually identical. We believe that this is due to the enhanced ion transport within the polymer film which increases the rate for both processes. Note also that the total amount of charge passed is the same for both processes. Table 1 summarizes the charge transport and charge capacity data for polypyrrole films of various thicknesses. Note that in all cases the fibrillar/microporous version is significantly faster than the conventional polypyrrole film and also has a greater charge capacity.

We can consider this enhancement in ion transport in terms of the morphological effect on ion transport in the polymer. Conventional electropolymerized polypyrrole films have a very dense amorphous morphology. This morphology has very poor ion transport characteristics. This is illustrated in part A of figure 8. In this morphology an ion must take a

long tortuous route through the polymer phase in which transport is very slow. In this morphology the distance an ion must be transported in the polymer phase can be quite large (ie. the thickness of the polymer film). A better morphology is illustrated in part B of figure 8. In this morphology solution channels which have fast ion transport have been incorporated into the film. However in this morphology the distance required for an ion to travel through the polymer phase can still be quite large. We believe that the ideal morphology is a fibrillar microporous one in which one has small diameter polymer fibrils surrounded by solution filled pores. This morphology is illustrated in part C of figure 8. In this fibrillar microporous film an ion will always be as close to solution as the radius of the polymer fibril.

## Conclusions

Polypyrrole with a well defined transport optimized morphology has been electrochemically prepared. This fibrillar/microporous version of polypyrrole shows significantly enhanced charge capacity and transport characteristics. The high fibril density and enhanced charge transport characteristics of polypyrrole synthesized in this fashion are attractive in battery applications of the polymer. We are presently pursuing this application.

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Table 1

# Summary of Charge-Transport Data for Reduction of Polypyrrole

Quantity of Polypyrrole (μmoles)	Approximate Thickness (μm)	Switching Time <sup>a</sup> (seconds)		Total Charge Available (mC)	
		flat <sup>b</sup>	fibrillar	flat <sup>b</sup>	fibrillar
0.44	0.5	3.1	1.6	8.8	10.0
0.88	1.0	6.0	2.2	18.6	20.0
1.31	1.5	6.5	3.4	28.0	34.3
1.75	2.0	10.2	4.4	39.2	45.3

<sup>a</sup> Time for 95% of charge to be delivered

<sup>b</sup> Conventional amorphous polypyrrole film

Table 1

# Gold / Anopore Composite Electrode

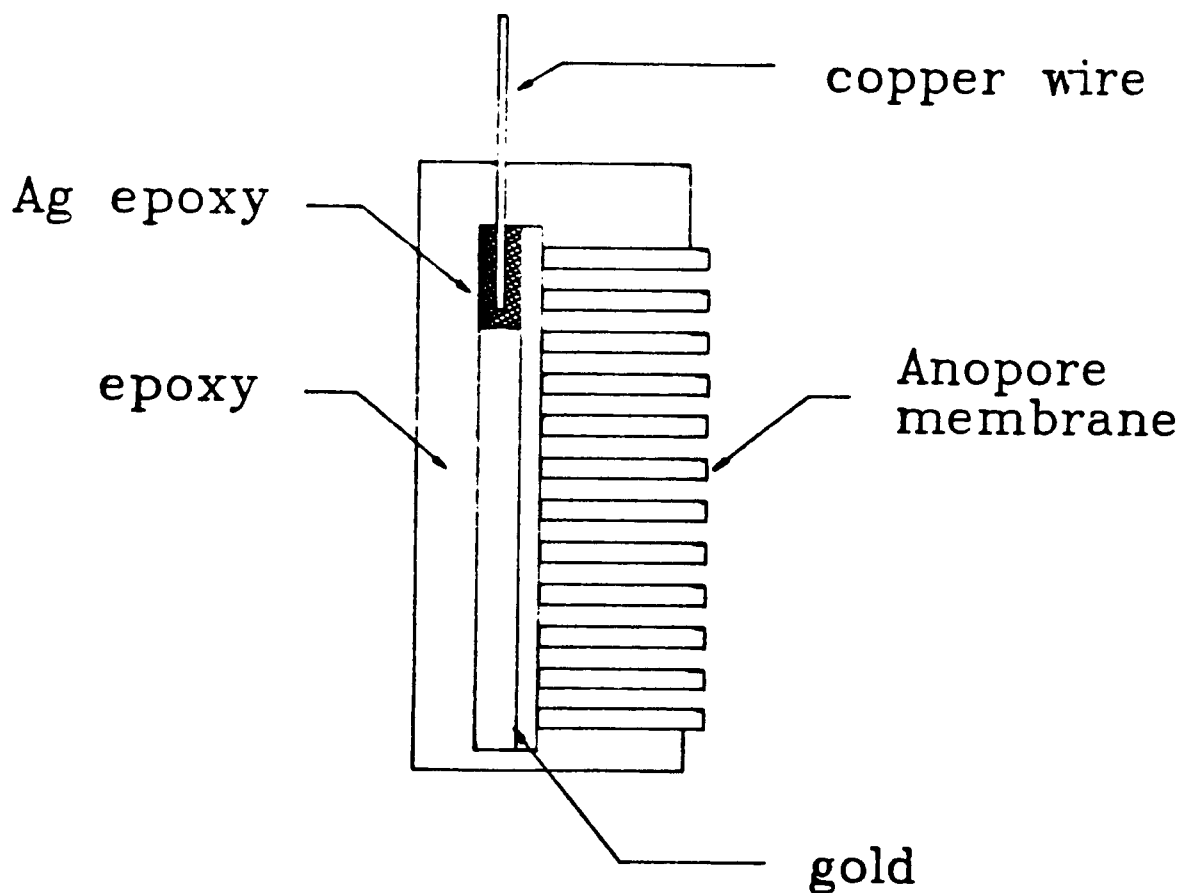
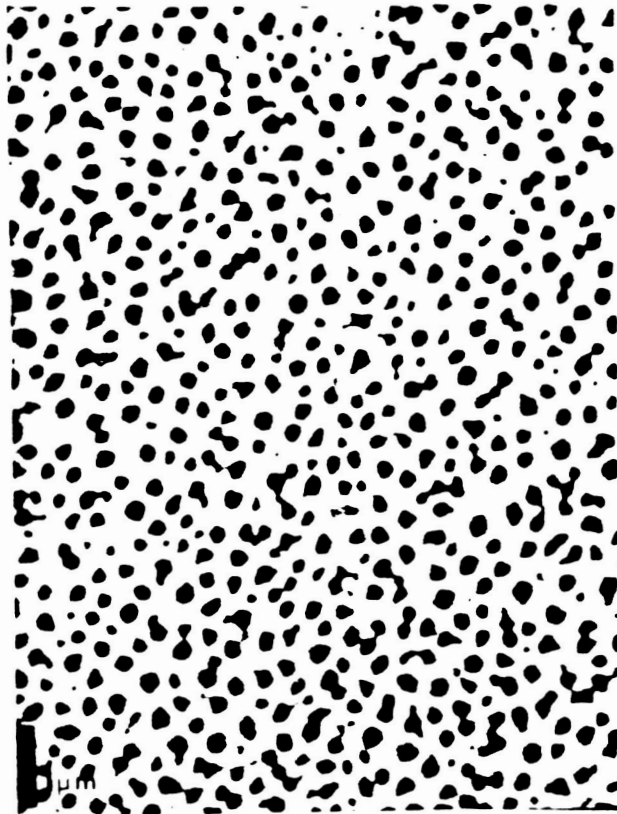


Figure 1



Electron Micrograph of 0.2 $\mu$ m Anopore Al<sub>2</sub>O<sub>3</sub>  
Filtration Membrane

Figure 2

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**Electron Micrograph of 2000 Å-Diameter Polypyrrole Fibrils  
Prepared Using Anopore  $\text{Al}_2\text{O}_3$  Membrane as the Host Material.**

**Bar = 1  $\mu\text{m}$**

**NOTE HIGH FIBRIL DENSITY**

Figure 3

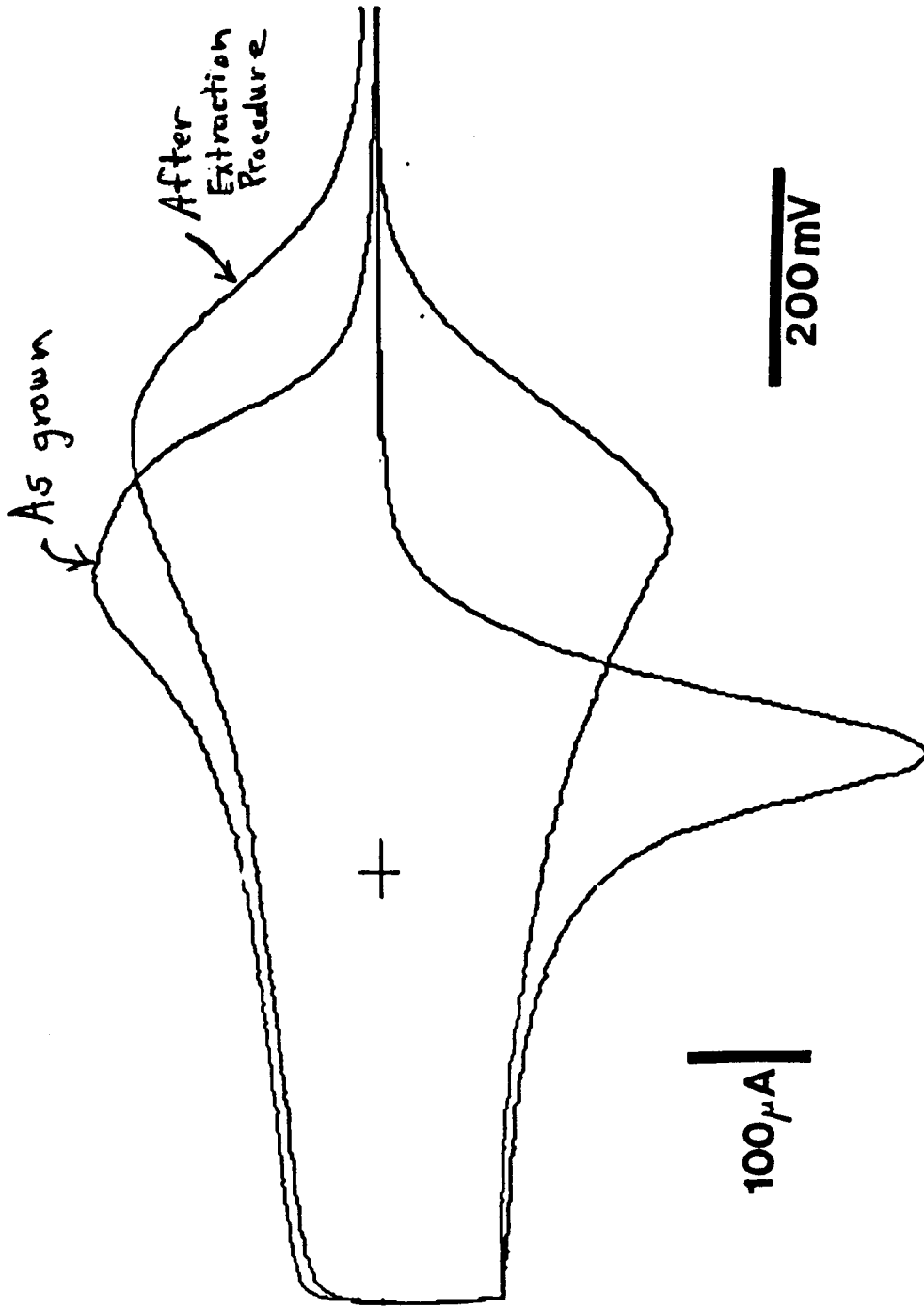


Figure 4

Scan rate 10mV/sec



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# UV-Vis Reflectance Spectra of Oxidized Polypyrrole

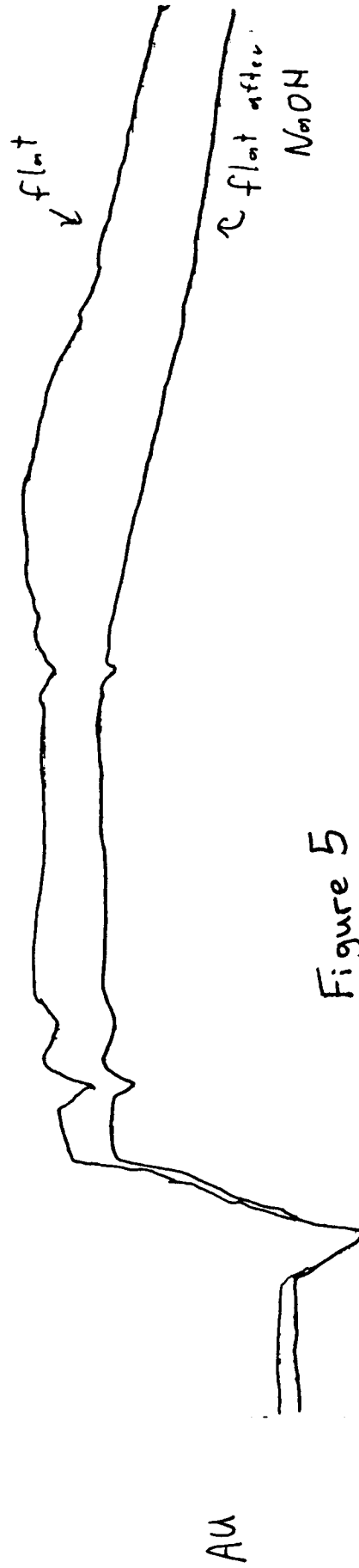


Figure 5

# Charge-Time Transients for a 1.0 micron thick Polypyrrole Film

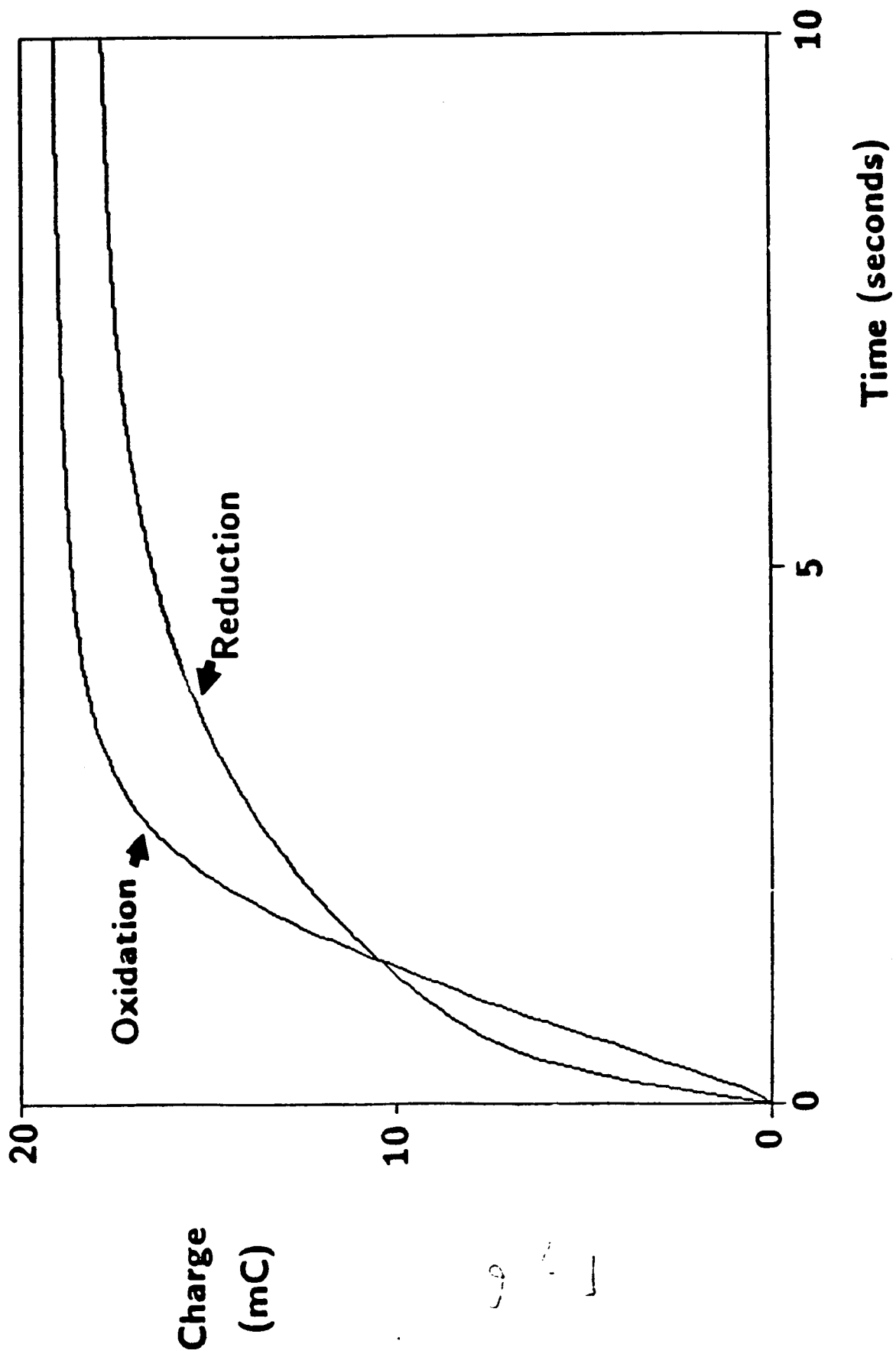


Figure 6

# Charge-Time Transients for a Microfibrillar/Microporous Polypyrrole Film

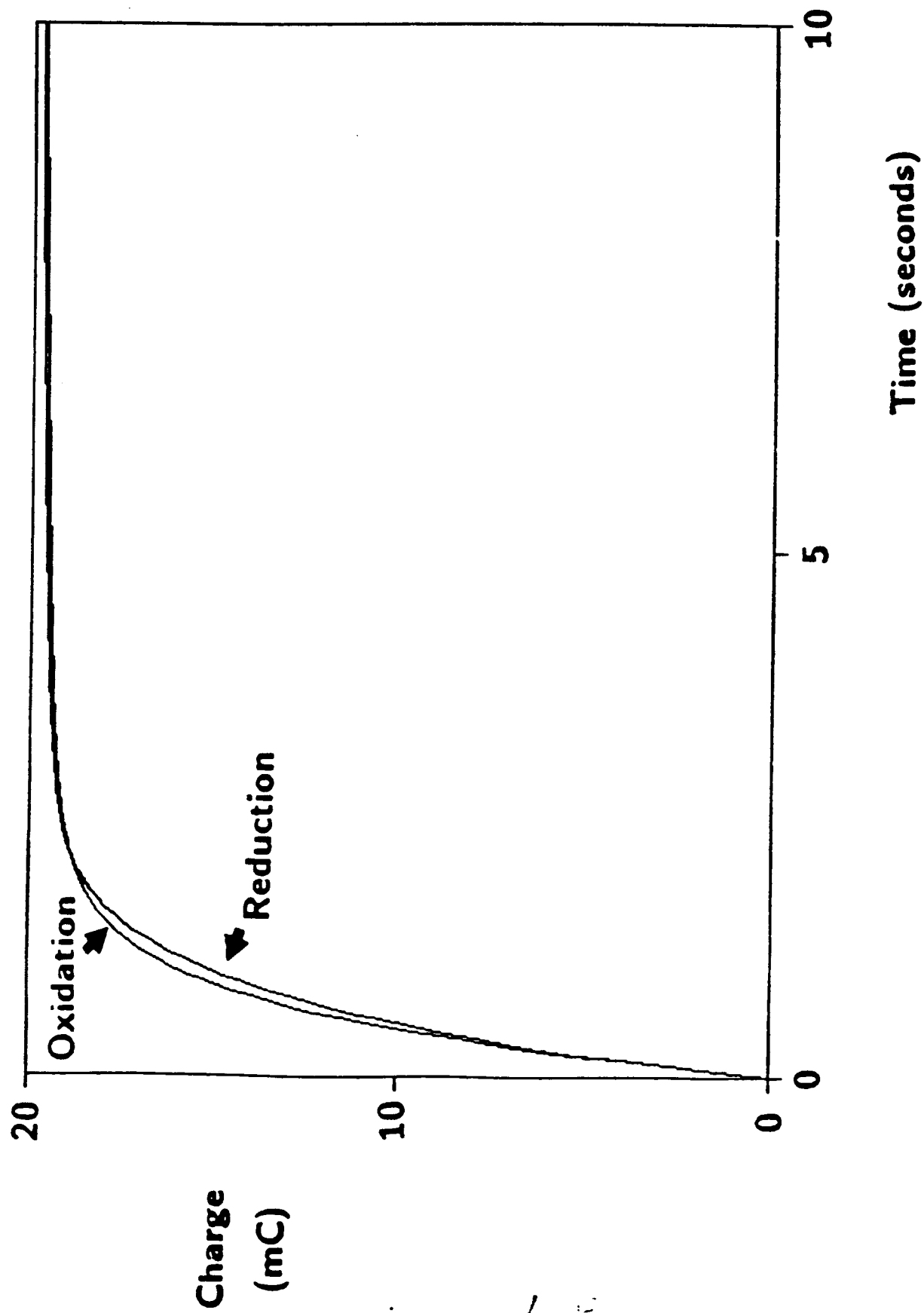
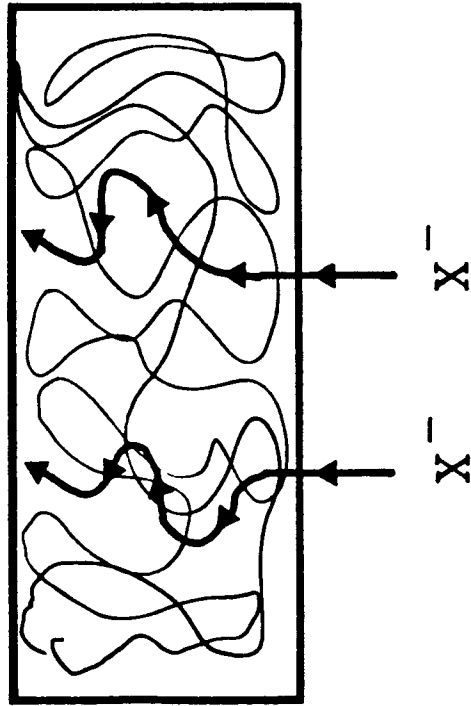


Figure 7

# "Cartoons" of Transport for Hypothetical Membrane Morphologies

## Amorphous Morphology

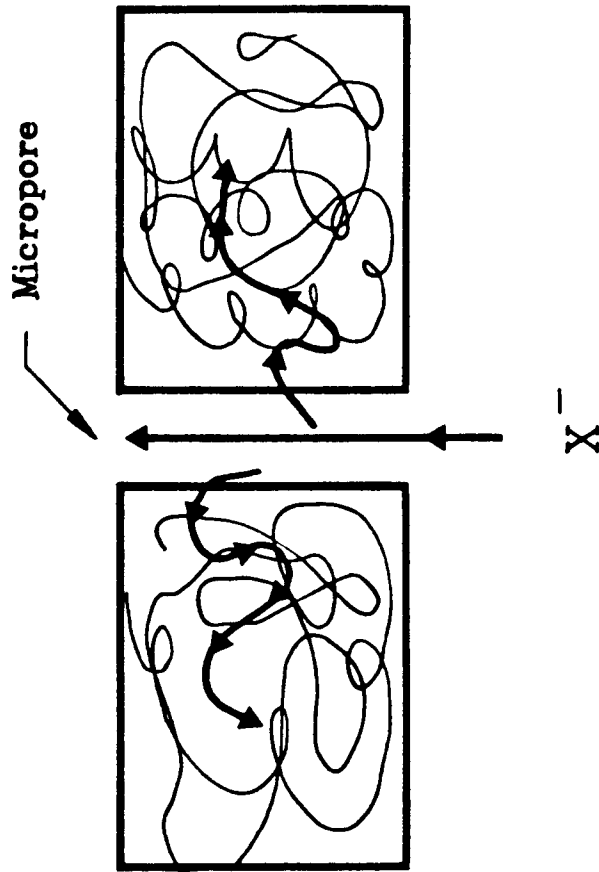


Diffusion path is  
tortuous, so  
transport is slow

BAD

Figure 8a

## Microporous Morphology

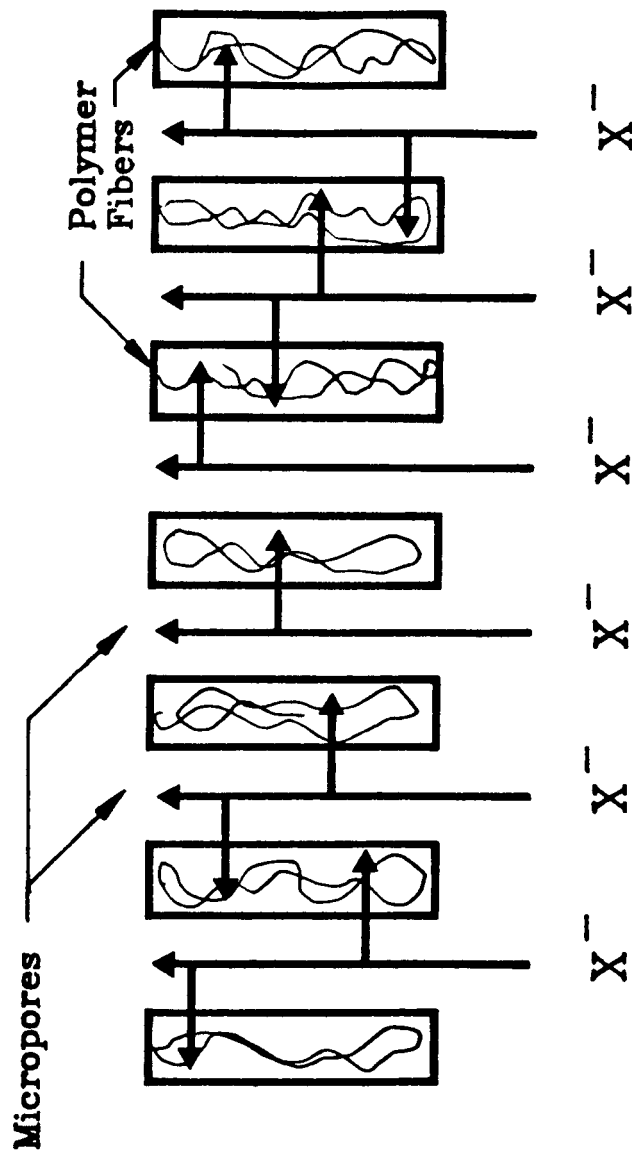


Pore transport is fast  
but polymer diffusion is  
extensive (and slow)

BETTER

Figure 8b

# Fibrillar/Microporous Morphology



Pore diffusion is fast and  
polymer diffusion is limited  
to narrow fibers

BEST

Figure 8c

## APPENDIX B

### MATHEMATICAL MODELING OF LITHIUM/POLYPYRROLE SECONDARY BATTERY CELL

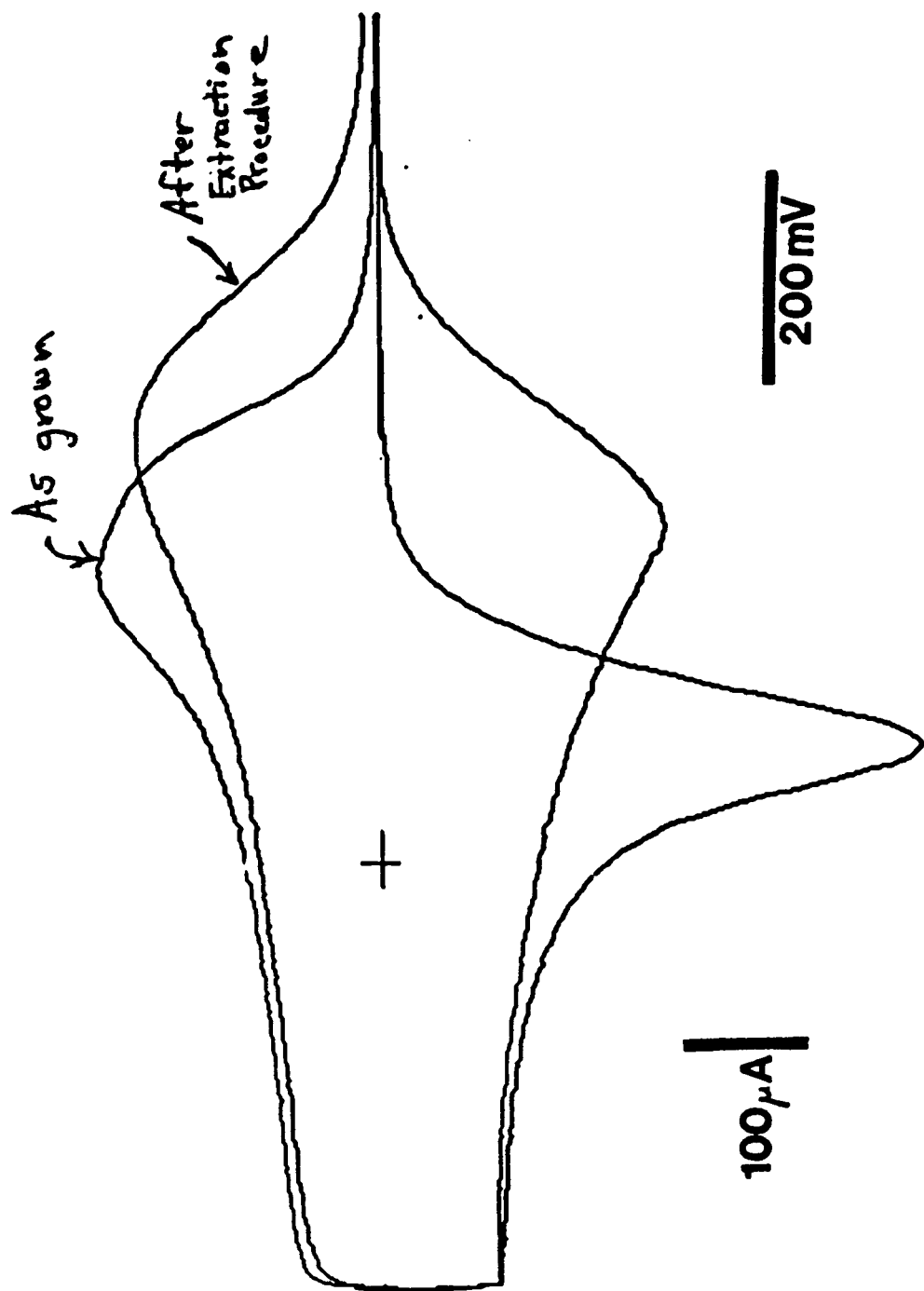


Figure 4

Scan rate  $10mV/sec$

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# UV-Vis Reflectance Spectra of Oxidized Polypyrrole

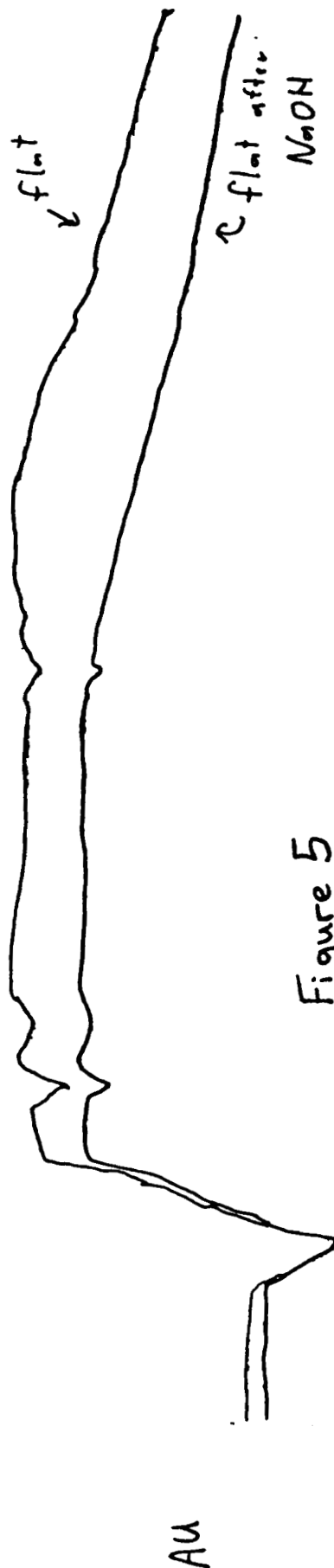


Figure 5

Wavelength	250	400.0	500.0	858.0
AU	1.0	1.0	1.0	1.0



# Charge-Time Transients for a 1.0 micron thick Polypyrrole Film

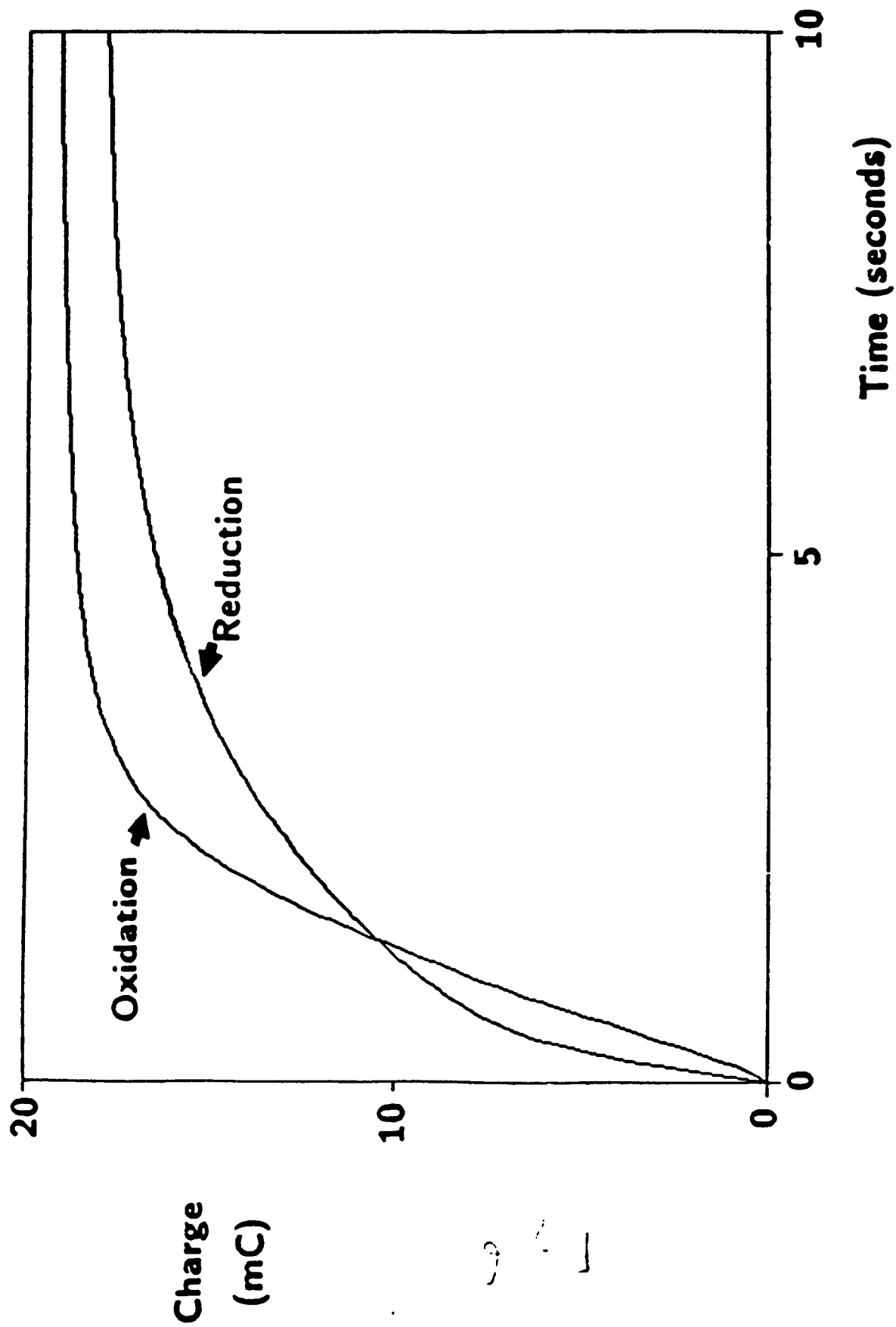


Figure 6

# Charge-Time Transients for a Microfibrillar/Microporous Polypyrrole Film

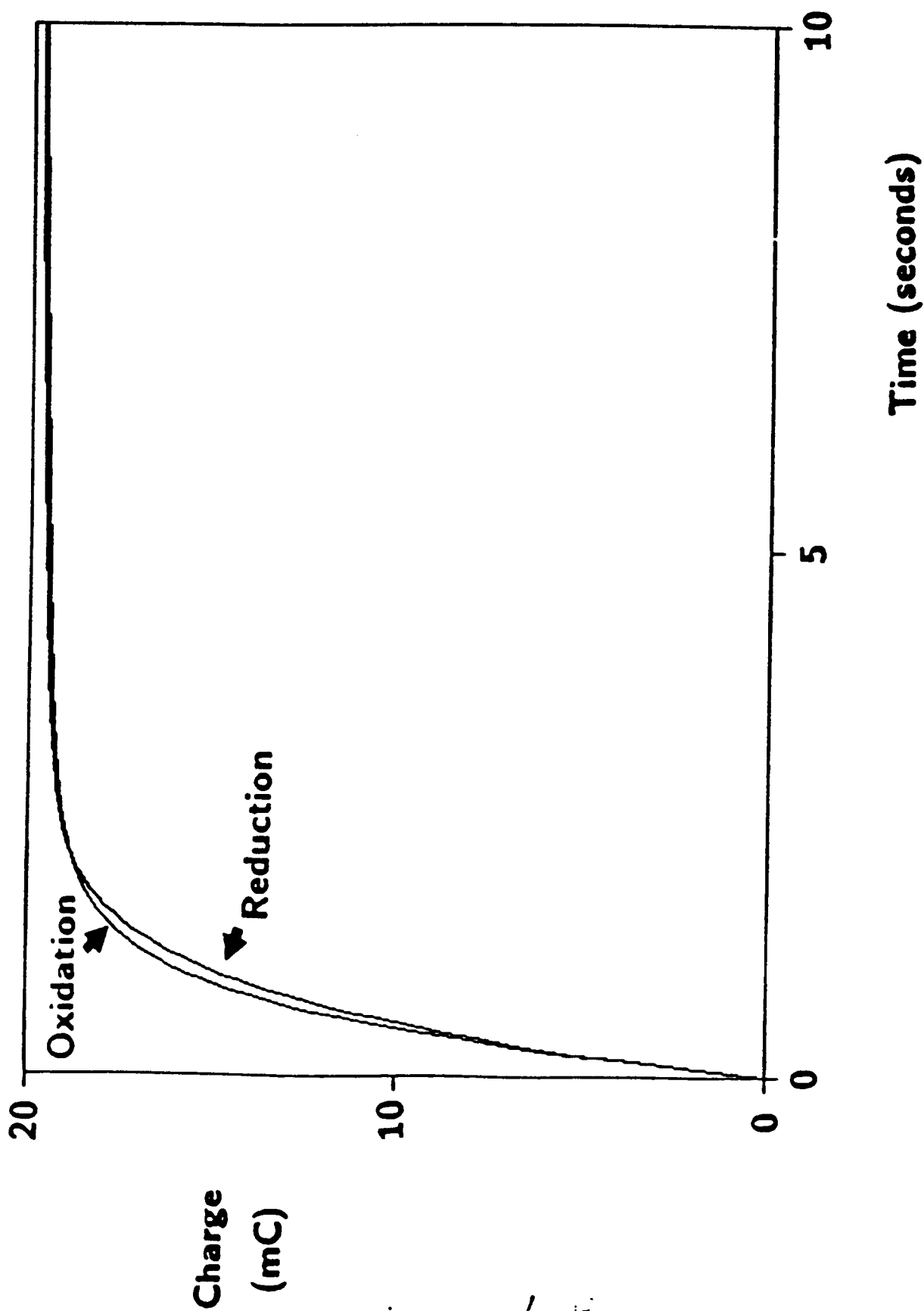
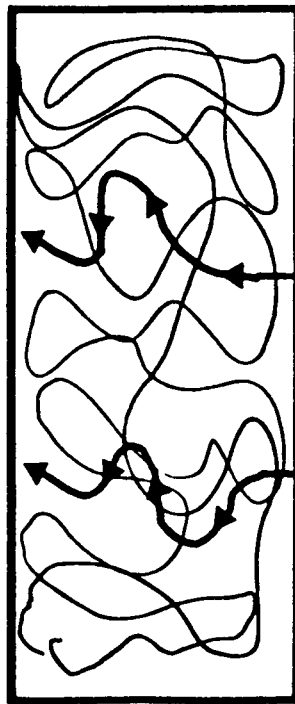


Figure 7

# "Cartoons" of Transport for Hypothetical Membrane Morphologies

## Amorphous Morphology



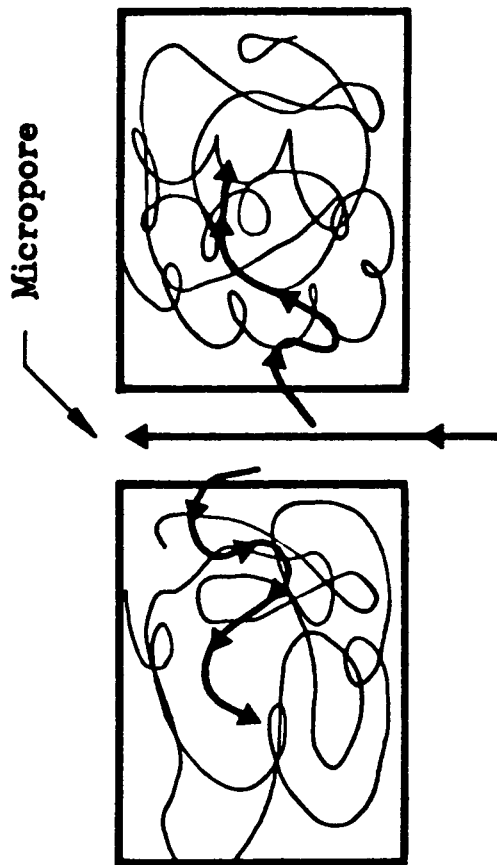
$X^-$   $X^-$

Diffusion path is  
tortuous, so  
transport is slow

BAD

Figure 8a

## Microporous Morphology

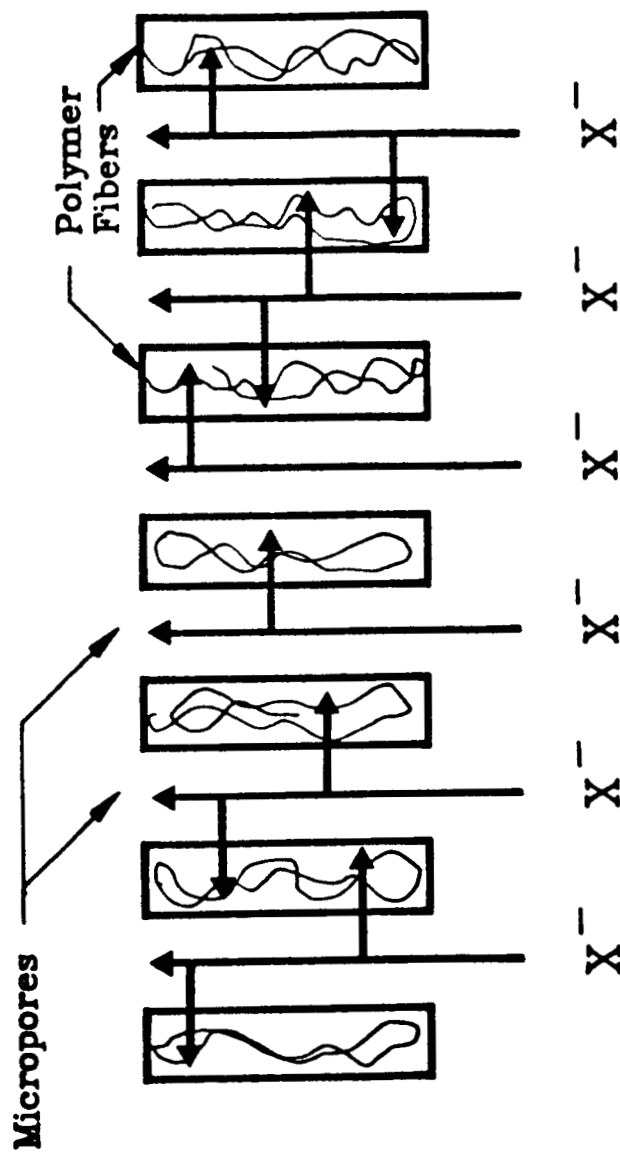


Pore transport is fast  
but polymer diffusion is  
extensive (and slow)

BETTER

Figure 8b

# Fibrillar/Microporous Morphology



Pore diffusion is fast and  
polymer diffusion is limited  
to narrow fibers

BEST

Figure 8c